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Cite as: AIP Conference Proceedings **1964**, 020048 (2018); https://doi.org/10.1063/1.5038330
Published Online: 15 May 2018

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Pressure Leaching of Chalcopyrite Concentrate

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Abstract. The results of chalcopyrite concentrate processing using low-temperature and high-temperature sulfuric acid pressure leaching are presented. A material of the following composition was used, 21.5 Cu, 0.1 Zn, 0.05 Pb, 0.04 Ni, 26.59 S, 24.52 Fe, 16.28 SiO_2 (in wt.%). The influence of technological parameters on the degree of copper and iron extraction into the leach solution was studied in the wide range of values. The following conditions were suggested as the optimal for the high-temperature pressure leaching: t = 190 °C, P_{O2} = 0.5 MPa, C_{H2SO4} = 15 g/L, L:S = 6:1. At the mentioned parameters, it is possible to extract at least 98% Cu from concentrate into the leaching solution during 100 minutes. The following conditions were suggested as optimal for the low-temperature pressure leaching: t = 105 °C, P_{O2} = 1.3-1.5 MPa, C_{H2SO4} = 90 g/L, L:S = 10:1. At the mentioned parameters, it is possible to extract up to 83% Cu from the concentrate into the leach solution during 300-360 minutes.

INTRODUCTION

Chalcopyrite ($CuFeS_2$) is one of the most abundant copper-containing minerals, which accounts for approximately 70 percent of the world's known copper reserves [1]. There are several different ways of chalcopyrite concentrates processing, but pyrometallurgical methods are classical and widely used. Concentrates treatment using a complex of furnaces is characterized by a number of environmental and technogenic problems, such as large emission of SO_2 and as a consequence, overproduction of sulfuric acid [2]. Thereby, the search studies of modern scientific laboratories focused on the development of hydrometallurgical technology, which will allow to arrange the most complete extraction of valuable components of the concentrate and to make the waste products of metallurgical process environment-friendly and sufficiently utilized.

Hydrometallurgical approaches to the processing of chalcopyrite concentrate include chloride leaching, bioleaching and oxidative autoclave leaching. The most attractive one, from economical point of view, is the pressure oxidative leaching, because it has a high kinetic parameters and high specific productivity [3-5]. The main aims of this paper are to show the efficiency and applicability of pressure oxidative leaching process for treatment of modern raw materials and set up the optimize conditions of this process for further development of hydrometallurgical technologies.

The problem of chalcopyrite concentrate processing using hydrometallurgical methods is the comparative resistance of chalcopyrite to treatment under atmospheric and pressure conditions, which is why, when processing mineral concentrates, it is necessary to create a high oxidation potential in the leaching system. Autoclave oxidative leaching is carried out by two different methods in the sulfuric acid media with the use of technical oxygen. The total chemical reaction of the high-temperature process is as follow:

$$2CuFeS_2 + 8.5O_2 + 2H_2O \rightarrow 2CuSO_4 + Fe_2O_3 + 2H_2SO_4 \quad (1)$$

The physical meaning of the equations is that heated and actively oxidized mineral - decomposes into iron, copper and sulfate ions (Reaction 2-3). Then, in the autoclave system, copper, iron sulfates and sulfuric acid are

Proceedings of the International Seminar on Metallurgy and Materials (ISMM2017)
AIP Conf. Proc. 1964, 020048-1–020048-5; https://doi.org/10.1063/1.5038330
Published by AIP Publishing. 978-0-7354-1669-7/$30.00

formed (Reaction 4-8). Iron (II) sulphate then oxidized to iron (III) sulphate, and the last compound undergoes to high-temperature hydrolysis, precipitating as hematite (Fe_2O_3) by the reactions 5-6 [6]:

$$CuFeS_2 + 4O_2 \rightarrow Cu^{2+} + Fe^{2+} + 2SO_4^{2-} \quad (2)$$
$$Cu^{2+} + SO_4^{2-} \rightarrow CuSO_4 \quad (3)$$
$$Fe^{2+} + SO_4^{2-} \rightarrow FeSO_4 \quad (4)$$
$$12FeSO_4 + 3O_2 \rightarrow 4Fe_2(SO_4)_3 + 2\ Fe_2O_3 \quad (5)$$
$$Fe_2(SO_4)_3 + 2H_2O \rightarrow 2FeSO_4(OH) + H_2SO_4 \quad (6)$$

Low-temperature oxidative pressure leaching has a similar chemical mechanism of chalcopyrite oxidation, but a special temperature conditions promote the elemental sulfur formation and sulfuric acid consumption, whereas under high-temperature conditions, the process is characterized by producing of sulfuric acid. The total chemical reaction of the low-temperature process is as follows:

$$CuFeS_2 + H_2SO_4 + 5/4\ O_2 + ½\ H_2O \rightarrow CuSO_4 + 2Fe(OH)_3 + 2S^o \quad (7)$$

The chemical mechanism of chalcopyrite leaching is based on the oxidation of sulfide sulfur by oxygen, while the released metal cations (Cu^{2+}, Fe^{2+}) interact with the sulfuric acid of the solution, forming copper and iron sulfates (Reaction 8). Then, ferrous sulfate under oxidizing conditions is oxidized to a ferric sulfate (Reaction 9) [7].

$$CuFeS_2 + 2H_2SO_4 + O_2 \rightarrow CuSO_4 + FeSO_4 + 2S^o + 2H_2O \quad (8)$$
$$FeSO_4 + ½\ H_2SO_4 + ¼\ O_2 \rightarrow ½\ Fe_2(SO_4)_3 + ½\ H_2O \quad (9)$$

Total course of the chemical reactions in the autoclave system requires optimally selected parameters (temperature, oxygen pressure, sulfuric acid concentration, etc.) that have a significant effect on the leaching intensity, the extraction of valuable substances, composition of leaching solutions and residues, pulp density, etc.

MATERIALS AND METHODS

A titanium autoclave with a capacity of 1 L was used. The chemical composition of the concentrate which was used in experiments is shown in Table 1. Chalcopyrite ($CuFeS_2$) and pyrite (FeS_2) were identified as the main phases. The material was analyzed by the following methods: atomic absorption, X-ray phase analysis and energy-dispersive X-ray spectroscopy.

Experiments on sulfuric acid pressure leaching were carried out according to the orthogonal plan of the experiment of the second order, using the «Statgraphics» program. The influence of different parameters (t °C, P_{O2} MPa, C_{H2SO4} g/L, T min) on the extraction of copper into the solution was studied.

TABLE 1. Chalcopyrite concentrate chemical composition, wt.%.

Cu	Zn	S	Fe	Pb	Ni	SiO2
21.5	0.1	26.59	24.52	0.05	0.04	16.28

RESULTS AND DISCUSSION

High-temperature pressure leaching

Experiments were carried out with the change of technological parameters within the following limits: t = 140-210 °C, P_{O2} = 0.1–0.6, C_{H2SO4} (initial) = 0-60 g/L, T = 90-180 min. Liquid to solid ratio keep constant (L:S = 6). Table 2 shows some of conditions and results of experiments on high-temperature pressure leaching of chalcopyrite concentrate.

An analysis of the obtained results showed that the presence of oxygen in the autoclave system is a fundamental factor of the mineral oxidation and extraction process. The intensity and completeness of decomposition of the chalcopyrite increases with growth of temperature. However, an increase in temperature above 190 °C does not give a significant effect on the copper extraction. The following parameters of the pressure leaching are proposed: t = 190 °C, P_{O2} = 0.5 MPa, duration = 120 minutes, initial concentration of the sulfuric acid up to 30 g/L.

TABLE 2. Parameters and results of the experiments (retention time = 90 minutes)

Temperature, °C	Partial oxygen pressure, MPa	Cu extraction, %
160	0,4	50
170	0,1	7
140	0,6	43
180	0,2	20
190	0,6	97
180	0,6	89
200	0,2	61
170	0,6	83
210	0,6	98
160	0,6	58

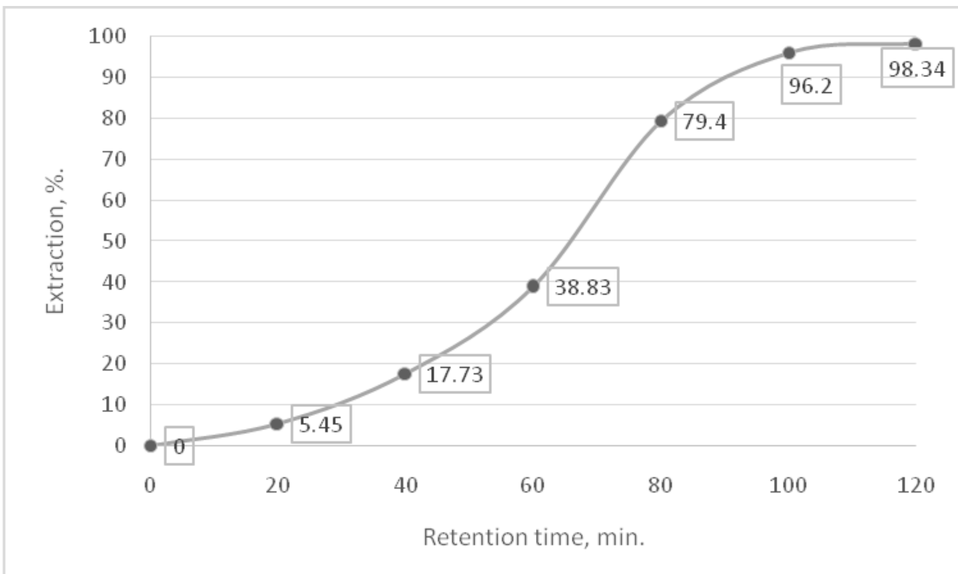

FIGURE 1. Dependence of copper extraction on leaching duration

An analysis of the graph in Fig. 1 showed that the increase in duration more than 120 minutes is not rational, since a significant portion of the copper passes into the solution in 90-100 minutes. The highest dissolution rate of copper is observed from 60 to 90 minutes from the beginning of the experiment.

In addition, in a number of experiments with a high initial concentration of sulfuric acid, the formation of a dense slurry, possibly silicic acid, was found, which greatly complicates the process of the leach solution filtration. Although, on the other hand, an increase in the concentration of sulfuric acid in the initial solution has a positive effect on the rate of copper extraction.

The residual iron content in the leach solution is 0.7-1.5 g/L. The remaining iron is precipitated in the form of hematite into a leaching residue, which has the following composition (in wt%): 31.01 Fe, 12.69 Si, 2.85 Ca. The yield of the leaching residue is 58%.

Low-temperature pressure leaching

Experiments were carried out with the change of technological parameters within the following limits: t = 90 – 113 °C, P_{O2} = 0.5-1.5, C_{H2SO4}(initial) = 60-150 g/L, T = 200-360 min. Liquid to solid ratio keep constant (L:S = 10). Table 3 shows some of conditions and results of experiments on low-temperature pressure leaching of chalcopyrite concentrate.

An analysis of the obtained results confirmed the need for initial sulfuric acid content close to the stoichiometric. The lack of acid leads to low copper extraction. At the same time, it is proposed to add acid with an excess factor of 1.2-1.3/1 for the most complete dissection and restriction of iron hydrolysis in the form of $Fe(OH)_3$. When a large excess of sulfuric acid is added (190 g/L), despite an insignificant increase in the intensity of the process, aggressive influence on the wall/stirrer surface of the autoclave is observed. Moreover, the same with case at the high-temperature conditions, high initial concentration of sulfuric acid in solution leads to the complicated filtration process. When adding the optimal amount of sulfuric acid, in the final leaching solution the concentration is at the level of 7-15 g/L.

The partial pressure of oxygen, in contrast to the initial concentration of sulfuric acid in the great extent effects on copper extraction. The intensity and completeness of extraction is proportional to the oxygen partial pressure, but its increase in excess of 1.5 - 1.7 MPa with low water vapor pressure can lead to the ignition of titanium [8].The temperature has less influence on the extraction level, but its increase to 110–113 °C reduces the performance. Such an effect can be associated with a reduced melting point of sulfur of some sulphide modifications[9].

Thus, it is recommended to conduct the process with the following parameters: t = 105°C, P_{O2} = 1.3 - 1.5 MPa, C_{H2SO4} = 70-100 g/L. Under such conditions, it is possible to extract up to 83% copper of the concentrate into the solution.

The yield of the leaching residue is 50%, which is consist from the elemental sulfur (~32 %), SiO_2 (~30%) and undissolved sulphides (~36%).

TABLE 3. Parameters and results of the experiments (retention time 300 min.)

Temperature, °C	Partial oxygen pressure, MPa	$C_{H2SO4(initial)}$, g/L	Cu extraction, %
90	1.2	150	46
95	0.6	90	31
100	0.2	90	11
105	1.4	75	80
110	0.6	90	45
113	1.4	150	60
113	0.5	75	48
110	1.6	120	72
105	0.5	30	7

Figure 2 shows the dependence of the duration of leaching on the copper and iron extraction. The course of the curve emphasizes the need for a minimum process retention time of 300 to 360 minutes, after which the iron content in the solution begins to fall due to the start of the hydrolysis process, which leads to some co-precipitation of copper.

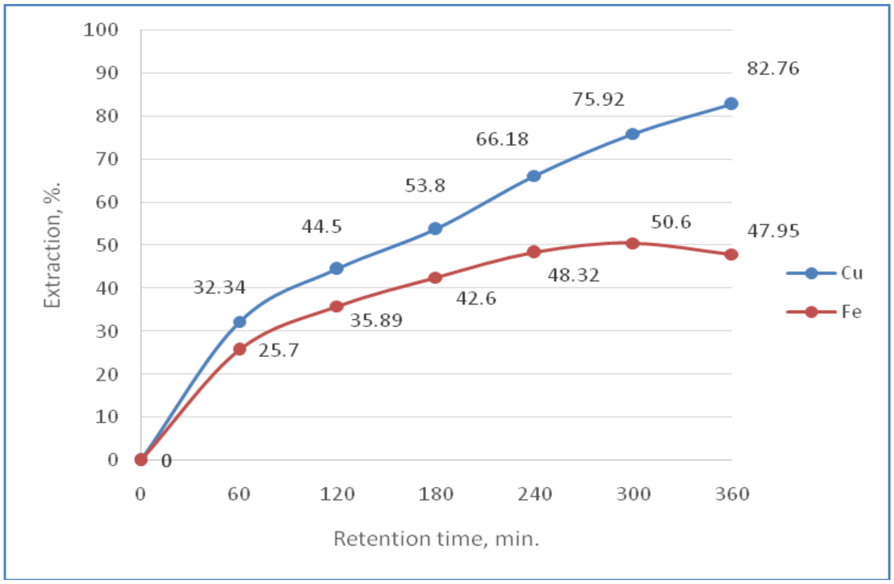

FIGURE 2. Change in the extraction of copper and iron from the duration of leaching

CONCLUSIONS

According to the studies, the most favorable conditions for the high-temperature pressure leaching were the following: t = 190 °C, P_{O2} = 0.6 MPa, retention time = 120 minutes, initial concentration of sulfuric acid 15-30 g/L. High-temperature pressure leaching allows to extract almost all the copper from the concentrate into the leaching solution while iron and precious metals remain in leaching residue. High leaching rate and low consumption of technical oxygen make this process very attractive for industrial application, but there is a significant problem with sulfate balance in the potential system-pressure leaching-electrowinning.

According to the studies, the most favorable conditions for leaching were found: t = 105-108 °C, P_{O2} = 1.3-1.5 MPa, retention time 300-360 min, initial sulfuric acid concentration 75-90 g/L. Low leaching rate, low copper recovery and high duration of the low-temperature process make it inapplicable in industrial scales nowadays. However, the process of elemental sulfur obtaining during the pressure leaching of chalcopyrite concentrate is reasonable. Further research is needed in the field of process intensification.

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